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PREPARATION AND PROPERTIES OF Ti-Y_2O_3 COMPOSITES FOR IMPLANT APPLICATIONS

The paper presents the preparation of Ti-(1-30wt.%)Y_2O_3 composites using the mechanical alloying process. Ti based materials are the best metallic biomaterials because of their excellent properties: biocompatibility, low Young moduli and high corrosion resistance. Pure Ti and Y_2O_3 powders were alloyed under argon atmosphere in shaker type mill (Spex 8000) followed by pressing and sintering.

The ultra-low grain size structure improves the mechanical properties and hardness of the new materials in comparison to microcrystalline Ti-based sinters. However, because of the porosity of approx. 20-30%, a decrease in the Young modulus is observed. Moreover, the new composites show good tendency towards covering by Ca-P compounds during soaking in SBF.

Keywords: Ti-based composites, yttrium oxide, mechanical alloying, biomaterials

1. Introduction

Titanium is one of the most important implant materials providing excellent properties, such as relatively low elastic modulus, low density, high strength and, obviously, long-life biocompatibility. There are, however, reports that show the accumulation of titanium in adjacent tissues, signifying metal corrosion in vivo [1,2]. As a result, these metal implants may lose [3-5]. Titanium and titanium based alloys have relatively poor tribological properties because of their low hardness and the elastic modulus is still higher than that of the bones [6]. One of the methods that allow changing the properties of Ti alloys is surface modification or production of composites exhibiting the preferred properties. The main ceramics used in the development of biomaterial are hydroxyapatite, bioglass or silica [7].

In the authors' previous work the Ti-10Y_2O_3 composite with a modified surface was investigated [8]. The aim of our current research was to develop and characterize the properties of a new generation of titanium-ceramic composites made from different amounts of yttrium oxide. Y_2O_3 is known as bioinert ceramic, but there are no reports about such composites containing wide range of yttria (1-30%). To develop the new materials the authors used the process of mechanical alloying, originally developed to produce oxide dispersion strengthened (ODS) alloys, including Y_2O_3 [9].

2. Materials and methods

Titanium-yttria nanocomposites with different contents of Y_2O_3 were prepared by mechanical alloying and the powder metallurgical process. The starting materials were Ti (325 mesh, 99.5%) from AlfaAesar and Y_2O_3 (325 mesh, 99.8%) from UBE Industries Ltd. The vial was loaded and unloaded in Labmaster 130 glovebox under high purity Ar atmosphere. The amount of powders was calculated and weighed using scales of the accuracy of 0.001 g. Mechanical alloying was performed under Ar atmosphere using the Spex 8000 shaker type mill for 24 h. The ball to powder ratio was 50:5 (50 g of steel balls and 5 g of powder). The milled nanocomposite powders were cold-pressed in a cylindrical die with the pressure of 1000 MPa using a uniaxial press machine. The green bodies were of the diameter of ϕ8 mm and the height of approx. 5 mm. All samples were sintered under Ar atmosphere at 1300°C for 60 min and chilled in the furnace to the room temperature.

The structure was analyzed using Panalytical Empyrean XRD with Cu Kα radiation and the microstructure was characterized by the Olympus microscope.

The SBF soaking test was applied to perform the measurements of the Ca-P compounds deposition. The samples were kept in Kokubo's solution (SBF) from 1 to 14 days in the New Brunswick Galaxy 14S incubator. The thermostat provided constant temperature of 36.6°C (temperature of the human body). The solution was refreshed every 24h to maintain a stable pH. The level of surface covered by Ca-P was examined using the

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Vega Tescan SEM and statistical measures were done using Microsoft Excel.

Compressive strength was measured at RT using the 4483 Instron mechanical testing machine, with the strain rate of 0.001^{-1}. The mechanical properties were measured on ten samples of each series.

3. Results and discussion

Titanium-yttria nanocomposites were prepared by mechanical alloying (MA) and the powder metallurgical process. The effect of MA on the composites was studied with the X-ray diffraction technique. The typical XRD patterns of Y_2O_3 and titanium before mechanical alloying are shown in Figs. 1a,b, respectively. During the MA process, the original sharp diffraction lines of the Ti and Y_2O_3 gradually became broader and their intensity decreased with the milling time (Figs. 1d,e). The peak broadening represents a reduction in the crystallite size and an increase in the internal strain in the mechanically alloyed materials. After 24 h of MA, the mixture of nanocrystalline particles formed in an amorphous matrix, without the formation of other phases – in Fig. 1e we can still observe peaks from the initial substances. Longer time of milling, with the other parameters unchanged, resulted in a similar effect – no further decrease of peaks intensity was observed, irrespective of the chemical composition. The formation of the bulk composites was achieved by cold uniaxial pressing and sintering. In all cases, the XRD analysis of Ti– Y_2O_3 composites showed the presence of Ti (hexagonal-type structure) and Y_2O_3 (Fig. 1f).

The microstructure of bulk composites was observed on samples mechanically polished and chemically etched with the Kroll's solution, as shown in Fig. 2. The small addition of Y_2O_3

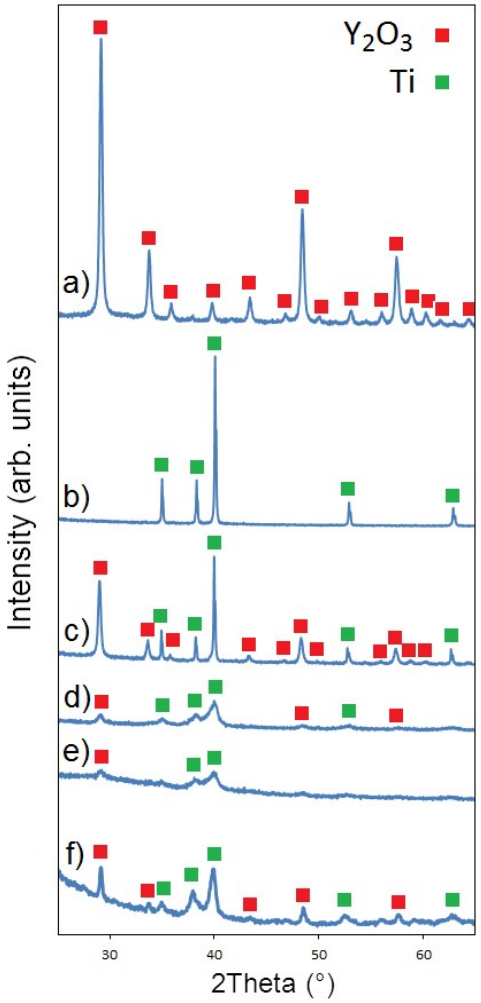

Fig. 1. XRD spectra of Ti and Y_2O_3 powders mechanically alloyed: (a) pure Y_2O_3, (b) pure Ti, (c) Ti-Y_2O_3 – 0h MA, (d) Ti-Y_2O_3 – 12h MA, (f) Ti-Y_2O_3 – 24h MA, (f) sintered composite. Spectra for Ti-20wt% Y_2O_3

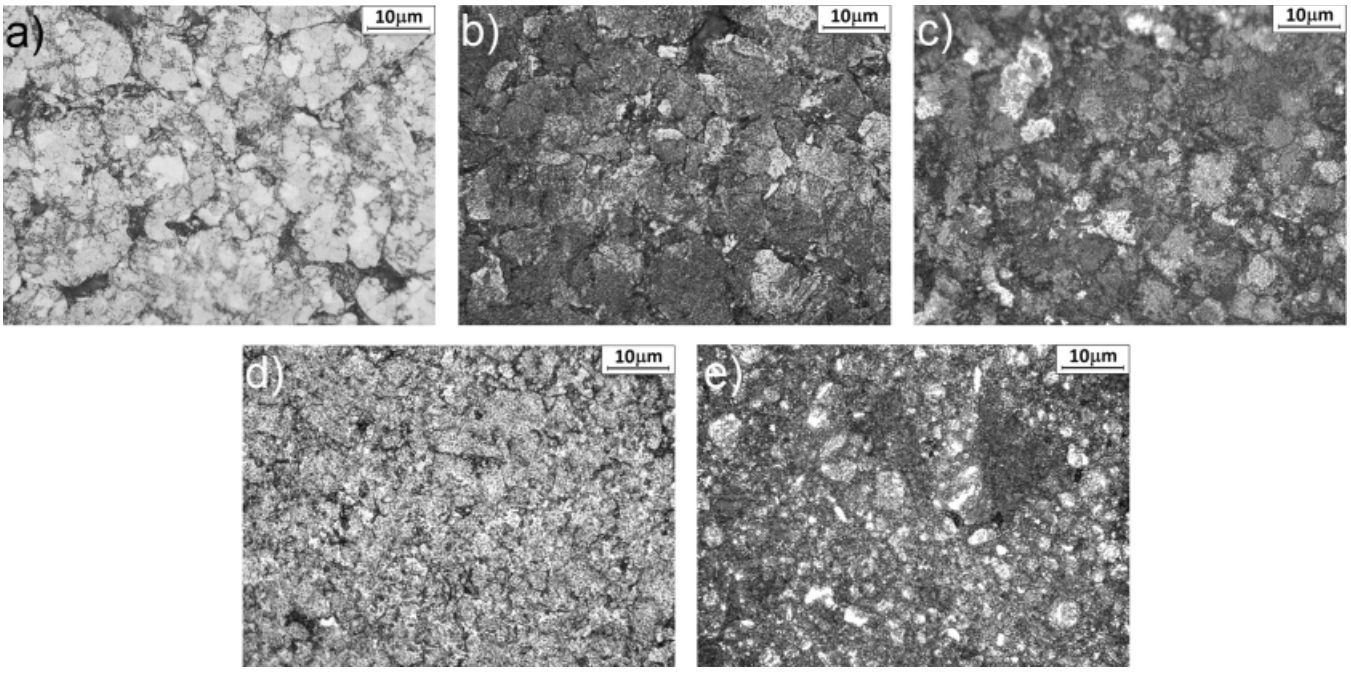

Fig. 2. Optical micrographs of sintered bulk a) Ti-1wt%Y_2O_3, b) Ti-5wt%Y_2O_3, c) Ti-10wt%Y_2O_3, d) Ti-20wt%Y_2O_3, e) Ti-30wt%Y_2O_3 composites

(1wt.%) had a relatively low influence on the grain size distribution. In this case (Fig. 2a), we could observe the a-Ti microstructure (typically for sintered titanium) with the grain size of approx. 1-5 μm in diameter. Increasing the yttria content resulted in a smaller grain size of the composites, which was approx. 1-5 μm and 0.2-1 μm for Ti-5% Y_2O_3 and Ti-30% Y_2O_3, respectively. Moreover, higher addition of the oxide phase (30wt.%) resulted in relatively big Y_2O_3 inclusions visible as white spots in Fig. 2e. We could also observe that there were evident pores in the microstructure. The general tendency is that the average porosity increases with the increasing yttria concentration from approx. 1% to 6%. Identical trend is observed for the pore size. The average porosity and pore size are shown in Table 1. An increase in the porosity leads to a deterioration of mechanical properties, yet, for biomedical applications, compressive stress and Young modulus should be comparable to those measured for the bones. For example, the Young modulus of the cortical bone is 15-20 GPa and that of the cancellous bone is 0.1-2 GPa. The compressive strength is 100-200 MPa for the cortical bone and 10-50 MPa for the cancellous bone [10].

Both, the increasing Y_2O_3 content and the porosity leads to decreasing elastic moduli and compression strength (Table 1) making those properties similar to those of the bone. The measured Young moduli were approx. 4 and 1.6 GPa for the composites with 5 and 30% of Y_2O_3, respectively. The sample with the 20% oxide content has the porosity 2% higher than

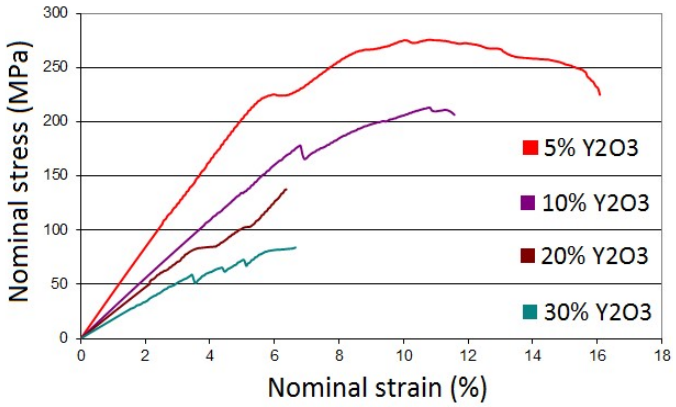

Fig. 3. Stress-strain curves for Ti-Y_2O_3 composites with different Y_2O_3 content

TABLE 1

Mechanical properties compared with the porosity and the pore size

Y_2O_3 content (wt%)	Average porosity (%)	Average pore size (μm)	Compression strength (MPa)	Elastic modulus (GPa)
5	1.1±0.2	4.5±0.4	308.2±3.7	4.21±0.09
10	4.7±0.1	8.1±1.2	238.3±2.6	2,75±0.03
20	6.0±0.3	20.7±4.1	145±1.6	2.02±0.02
30	3.9±0.2	19.8±4.8	89.6±2.8	1.69±0.07

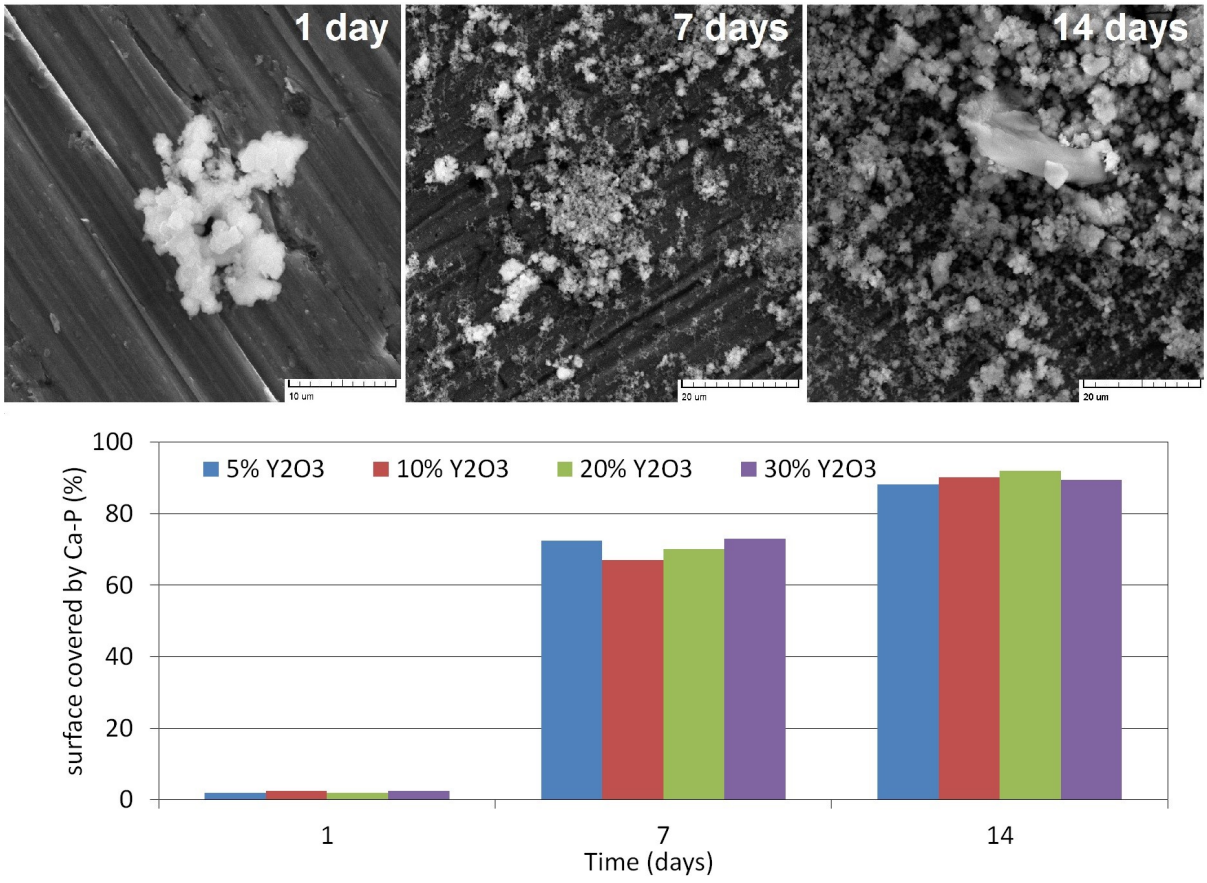

Fig. 4. The SBF soaking test results: SEM pictures of Ca-P compounds deposited on the Ti-10Y_2O_3 surface after 1, 7 and 14 days and data related to the surface covered by Ca-P for all composites after the same periods

Ti-30%Y_2O_3, but the elastic modulus is lower for the second one. The porosity is a very important factor in the E reduction. Our results show a significant influence of the chemical composition of biomaterials on the improvement of mechanical properties.

The SBF soaking test was applied to perform the measurements of the Ca-P compounds deposition. The samples were kept in SBF from 1 to 14 days. All new composites showed a good ability towards covering by the Ca-P compounds during soaking, which suggests good biocompatibility with the human body. After one week, the surfaces were covered in more than 60% and after 2 weeks almost in 90%. The ultrafine-grained Ti-Y_2O_3 show a better ability towards covering by Ca-P in comparison to pure microcrystalline Ti.

4. Conclusions

In this paper, the authors studied the structure, the microstructure, the mechanical and physico-chemical properties of Ti-Y_2O_3 ultrafine-grained composites prepared by mechanical alloying and powder metallurgy. The studies have led to the following conclusions:

1. Mechanical alloying is an effective method of Ti-Y_2O_3 composites preparation.
2. Increasing the amount of Y_2O_3 results in:
   - ultrafine-grained microstructure,
   - increasing porosity level,
   - a negative effect on the mechanical strength but a desirable decrease of the Young modulus.
3. The new composites show good ability towards covering by Ca-P compounds during soaking in SBF, which suggests a good biocompatibility with the human body.

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